

## PREDICTION OF THE PHASE COMPOSITION OF GLASS-FORMING BATCHES

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Glass-forming batch components were synthesized in an aqueous medium. The pH method was used to control the processes. Based on a relative analysis of pH curves, the phase composition of the products of synthesis was predicted, which was substantiated by x-ray and IR spectral analysis.

Analysis of the phase composition of batches is a complicated time-consuming process requiring expensive equipment (diffractometers, spectrometers, etc.), which are not found in every laboratory. However, knowledge of phase composition is necessary for studying the structure and properties of glasses, primarily of glasses designed according to nonstandard methods, for instance, to make microspheres used as gas microballoons. For this purpose, pH-metry was used in an attempt to predict the phase composition of batches produced by the sol-gel method using comparative analysis of pH-curves.

A batch of the composition  $\text{Na}_2\text{O} - \text{PbO} - \text{SiO}_2 - \text{H}_8\text{C}_6\text{O}_7 - \text{H}_2\text{O}$  ( $\text{PbCANAi}$ ) was synthesized in an aqueous medium and a complex mixture of products was obtained. In this context specific subsystems  $\text{PbO} - \text{H}_8\text{C}_6\text{O}_7 - \text{H}_2\text{O}$  ( $\text{PbCA}$ ),  $\text{Na}_2\text{O} - \text{SiO}_2 - \text{H}_8\text{C}_6\text{O}_7 - \text{H}_2\text{O}$  ( $\text{CANAi}$ ), and  $\text{Na}_2\text{O} - \text{SiO}_2 - \text{H}_2\text{O}$  ( $\text{aqNaSi}$ ) were investigated. The initial materials were silicic acid  $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ , citric acid  $\text{H}_8\text{C}_6\text{O}_7$  ( $\text{CA}$  – *citric acid*), sodium hydroxide  $\text{NaOH}$ , and lead oxide  $\text{PbO}$  of the grade “analytically pure.” The obtained solutions were dried at the ambient temperature.

Synthesis of  $\text{PbCANAi}$  was carried out first in an acid and then in an alkaline medium. A CA solution ( $\text{pH} = 2$ ) was added to  $\text{PbO}$  powder ( $\text{pH} = 5.5$ ) under heating and intense stirring, as a consequence of which a viscous suspension ( $\text{PbCA}$ ) was formed, which stuck to the electrodes of the pH-meter and could be separated only by the mechanical means. This distorted the readings of the instrument and motivated the use of a universal paper indicator.

The suspension was dissolved in  $\text{aqNaSi}$  solution ( $\text{pH} = 12$ ) obtained at approximately  $100^\circ\text{C}$ . Following the uniformity principle, pH in synthesis of the main system and its subsystems was measured using the paper indicator. The

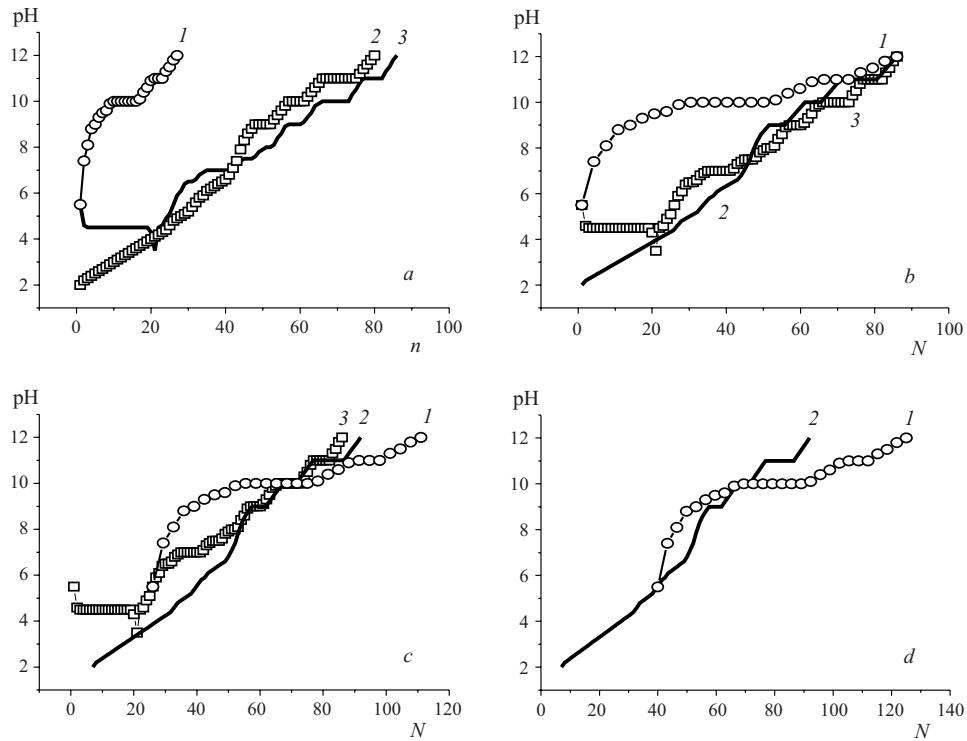
pH reference scale was graded in integer values; however, in the case of transitional colors pH values were taken as the arithmetic mean. For instance, when the yellow color correlated with  $\text{pH} = 6$  and the green color correlated with  $\text{pH} = 7$ , in the case of a yellow-green color, pH was taken equal to 6.5. Random values (“noise”) were eliminated by smoothing: an arithmetic mean (smoothed) value was calculated based on four consecutive pH values; all data were processed separately for each synthesis with an interval equal to 1. The smoothed values were used to construct pH curves. An example of the procedure of smoothing experimental pH values in synthesis of  $\text{CANAi}$  is shown in Table 1.

The curve  $\text{PbCANAi}$  is formed by two branches (Fig. 1a): the “acid” branch is descending ( $\text{pH} = 5.5 – 3.5$ ) and the “alkaline” branch is ascending ( $\text{pH} = 3.5 – 12$ ). The first branch consists of two S-shaped segments divided by an

TABLE 1

Aliquot	pH value	
	measured	smoothed
1	2	–
2	2	–
3	2	–
4	2	2
5	2.5	2.1
6	2.5	2.2
7	2.5	2.4
8	2.5	2.5
9...	3...	2.6...
77	12	11
78	12	11
79	12	11.1
80	12	11.2
81	–	11.5
82	–	11.8
83	–	12

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**Fig. 1.** pH curves of reaction between glass-forming mixture components and dissociation of sodium silicate in water: *a* and *b*) real and normed pH curves, respectively; *c* and *d*) superposed curves after normalization; 1) aqNaSi; 2) CANaSi; 3) PbCANaSi; *n*) quantity of solution aliquots added; *N*) normed quantity of aliquots.

extended horizontal at pH = 4.5. This indicates that two substances are synthesized in the reaction between PbO and CA and a buffer solution is formed at pH = 4.5, since acid was added, but the pH value did not change. When CA was added after pH = 3.5, a second horizontal was formed ending with a sharp break before pH = 2 (acid pH), i.e., a second buffer solution was formed, which was not the aim of synthesis. The reaction of PbO with CA was terminated at pH = 3.5.

The conclusions from analysis of the shape of the “acid” branch agree with data in [1] on formation of lead hydro- and dehydrocitrates. The “alkaline” branch has a more complicated shape: it consists of several S-shaped segments. To interpret this shape, the reaction of CA with CANaSi solution and its dissociation in water (aqNaSi) was investigated. The process ended at pH = 12 (the end solution). The reactions proceed at different velocities; therefore, the curves had different lengths (Fig. 1*a*). Due to noise, the pH values can be considered random and normalization [2] is applied to them: by selecting the respective coefficients the curves were reduced to a 100% size taken as the length of the longest pH curve, i.e., PbCANaSi (Fig. 1*b*):

$$A_i = \frac{a_i n_{\max}}{n_i},$$

where *A* and *a* are the normed and the real pH values; *n* is the curve length equal to the quantity of aliquots of the respec-

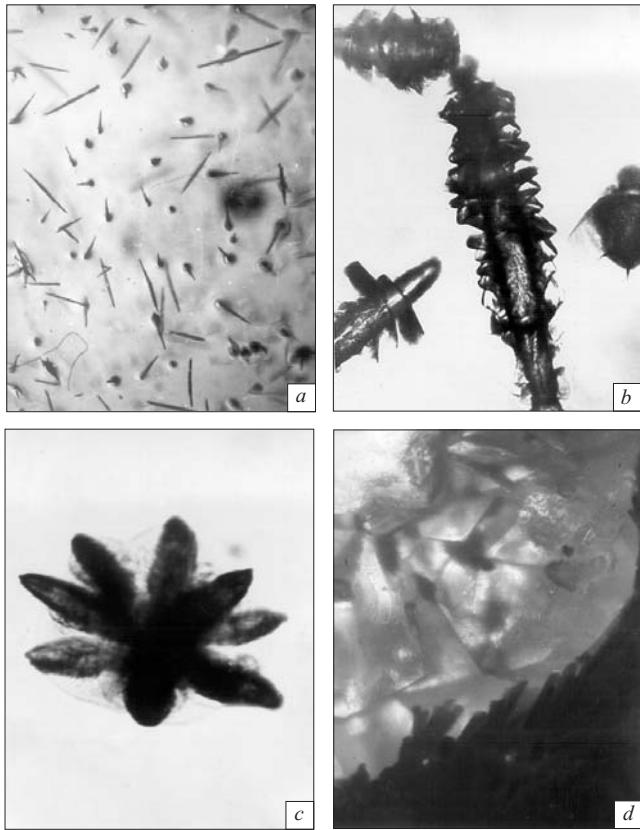
tive component solution; the index *i* is the normed curve; the index *max* is the longest curve.

Considering that the curves CANaSi and aqNaSi belong only to the “alkaline” range and the curve PbCANaSi belongs both to the acid and the alkaline ranges, the initial points of the first curve were superposed on the points of the curve PbCANaSi (Fig. 1*c*), in which the analogous pH coincided. The curve aqNaSi was displaced in such a way that its initial point indicating the start of sodium silicate dissociation coincides with the respective point on the curve CANaSi (Fig. 1*d*). The displacement coefficients *k*<sub>displ</sub> were calculated from the formula

$$k_{\text{displ}} = n_{\text{pH, max}} - n_{\text{pH, } i},$$

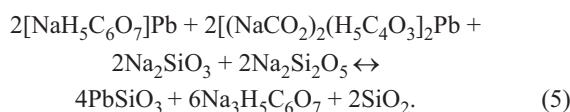
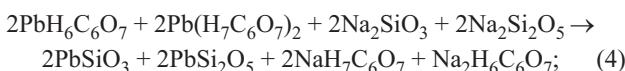
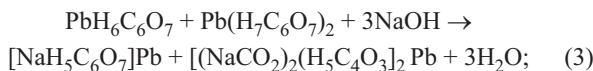
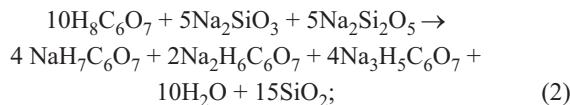
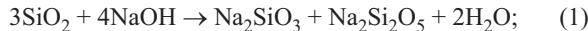
where *n* <sub>pH</sub> is the number of the aliquot with the respective pH.

At pH = 8–11 (Fig. 1*c*) the normed curves PbCANaSi and CANaSi coincide, although until then they have been apart. Coincidence with the curve aqNaSi occurs within the interval of pH = 5.5–6.4 and on the horizontal segment at pH = 10.0. The sodium-silicate solution contains OH<sup>–</sup> anions, which create an alkaline background for reactions [3]. Up to a value of pH = 6.4, the curves are rather steep as aqNaSi solution is added to the citrate medium, which points to a high rate of reaction causing the variation of pH from 3.5 to 6.4: the angles (Fig. 1*b* and *c*)  $\alpha_{\text{PbCANaSi}} \approx \alpha_{\text{CANaSi}} \approx 70^\circ$ . Reaching the value pH = 5.5–6.4 can be attributed to the neutralization of acid.



**Fig. 2.** Photos of crystals formed in gel and in dry material: *a*) lead silicate crystals ( $\times 7$ ) ; *b*) growing lead silicate crystal ( $\times 23$ ); *c*) crystalline cluster ( $\times 23$ ); *d*) crystalline phases of sodium silicate ( $\times 23$ ).

Synthesis of lead silicates proceeded in an alkaline medium by a multi-stage mechanism, which is confirmed by the shape of the curve PbCANaSi consisting of several S-shaped segments. Some of the probable reactions indicating the complexity of the phase composition of batches are listed below:



The reaction of tribasic CA with aqNaSi was accompanied by the formation of three salts, which is responsible for

the shape of the curve CaNaSi [equation (2)]; emerging  $\text{SiO}_2$  could not perceptibly change the shape of the curve, since sodium mono- and disilicate were formed (1) in reaction with  $\text{NaOH}$ , and the same could happen as a consequence of the formation of  $\text{SiO}_2$  (5). The reaction of lead citrate with aqNaSi can result in the formation of lead silicate and sodium mono- and disilicates (4), as well as sodium plumbocitrates (3), which are intermediate substances in the formation of lead silicate and sodium citrate (5).

This can be interpreted as follows. After the end of the acid stage, lead citrates were in the precipitate and dissociated sodium silicates were in the solution. Lead citrates were complicated due to association of  $\text{Na}^+$  cations instead of carboxyl group hydrogen. This process could go on while the intensity of the field of  $\text{Na}^+$  cations was insufficient to break the lead – carboxyl oxygen bond. Then the  $\text{Pb} - \text{O}$  bonds broke, and  $\text{PbSiO}_3$  and sodium citrates were formed: monosodium citrate up to  $\text{pH} = 9.0$ , disodium citrate up to  $\text{pH} = 10.0$ , and trisodium citrate up to  $\text{pH} = 11.3$ . The coincidence of the curves PbCANaSi and CANaSi at  $\text{pH} = 8.0 - 11.3$  (Fig. 1c) indicates the similarity of the processes determined by synthesis of alkaline citrates. The divergence of the curves in the range of  $\text{pH} = 6.4 - 8.0$  is presumably due to the formation of complexes.

Most probably there were more reaction products than those indicated in the reaction schemes, in view of the probability of formation of citrate complexes, silicates of varying stoichiometry, hydroxy compounds, and aqua-complexes. However, the most probable is the formation of  $\text{Na}_2\text{SiO}_3$ ,  $\text{Na}_2\text{Si}_2\text{O}_5$ ,  $\text{PbSiO}_3$ , sodium citrates, and  $\text{SiO}_2$ , and also  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$ , since the final solution was dried in air.

Figure 2 shows photographs of crystalline phases formed in gel and in dry material: a panorama of needle-shaped crystals of lead silicate at the stage of a moist transparent gel, the shadow picture of the material approaching the growing crystal accompanied by rotation (the formed part rotates more slowly than the growing part, as the trace typical of an object rotating in a liquid was absent), a conglomerate of crystals, and crystalline phases that were preceded by drop liquation.

Dried material was analyzed using a Dmax/RC x-ray diffractometer (Japan). A computer program developed on the basis of the database in [4] was used to identify phases. The presence of  $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ ,  $\text{Na}_2\text{Si}_2\text{O}_5$ ,  $\text{Na}_2\text{Si}_4\text{O}_9$ ,  $\text{Na}_4\text{SiO}_4$ ,  $\text{Na}_6\text{Si}_2\text{O}_7$ ,  $\text{Na}_6\text{Si}_8\text{O}_{19}$ ,  $\text{PbSiO}_3$ , and  $\text{Na}_2\text{CO}_3$  was reliably registered. Some phases were not identified due to the limited size of the database. It was established that the needle-shaped crystals are  $\text{PbSiO}_3$  and the crystalline phases after liquation are  $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ ,  $\text{Na}_2\text{Si}_2\text{O}_5$ , and  $\text{Na}_2\text{CO}_3$ .

The dry residue was subjected to IR-spectral analysis in the range of  $5000 - 400 \text{ cm}^{-1}$  using a UR-20 spectrophotometer: the analyzed residue was compressed in a KBr matrix and the spectra underwent computer processing. Based on the analysis results (Table 2), one can infer the presence of lead and sodium metasilicates, sodium disilicate, sodium car-

TABLE 2

Absorption band, $\text{cm}^{-1}$	Reason for emergence of the band in spectrum	Published source
1420 – 1405, 1605 – 1600	Symmetric and asymmetric valence vibrations of C – O 1.5-bonds in $\text{COO}^-$ -groups of citrate anions (corroboration of synthesis of sodium and/or lead citrates)	[5]
3306 – 3193	Valence vibrations of OH groups associated with citrates	[5]
	Valence vibrations of O – H bond in $\text{COOH}$ groups (indicate formation of citric acid as impurity in decomposition of silicocitrates in solution drying)	[6]
1560 – 1370, 850	Formation of $\text{Na}_2\text{CO}_3$	[7]
3620 ( $\nu_4$ ), 3510 ( $\nu_3$ )	Emergence of cyclic structures due to silanol OH-groups	[8]
3400 – 3380	Adsorbed water	[9]
3310 – 3240	Vibration of H – OH bond in crystal-hydrate water	[10]
1650 – 1620	Deformation vibrations of OH bond in water molecule $\text{H}_2\text{O}$	[11]
1007, 962, 915, 1420 – 1405, 1035 – 1020, 880, 765 – 750	Formation of metasilicate $\text{PbO} \cdot \text{SiO}_2$	[7]
1120 – 1100, 1070 – 1030, 800, 780	Polymers formed by tetrahedra $[\text{SiO}_4^-]$	[7]
1200 – 980	Formation of a three-dimensional structure of $[\text{SiO}_4^-]$	[7]
1450 – 1440, 1115 – 1100, 1035 – 1020, 980 – 970, 905 – 895, 880 – 870, 770 – 760	Formation of metasilicate $\text{Na}_2\text{O} \cdot \text{SiO}_2$ , superposition of absorption bands of $\text{PbO} \cdot \text{SiO}_2$ in ranges of 1115 – 1100 and 1035 – 1020 $\text{cm}^{-1}$	[7]
1085, 980 – 970, 765 – 750	Formation of disilicate $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ , superposition of absorption bands $\text{Na}_2\text{O} \cdot \text{SiO}_2$ at 980 – 970 $\text{cm}^{-1}$	[7]
1053 – 1042	Local heterogeneity area with intermediate composition from $\text{Na}_2\text{O} \cdot 3\text{SiO}_2$ to $\text{Na}_2\text{O} \cdot \text{SiO}_2$	[7]
914 – 940	The same from $3\text{Na}_2\text{O} \cdot \text{Si}_2\text{O}$ to $2\text{Na}_2\text{O} \cdot \text{SiO}_2$	[7]

bonate, alkali silicates of other stoichiometry, and free citric acid as impurity phases; water was present in the form of OH groups and in the molecular form (crystal-hydrate and adsorbed water).

Thus, the x-ray and IR spectral methods mostly corroborate the phase composition of the batch predicted as a consequence of comparing the pH curves. This substantiates the possibility of its practical application in liquid-phase synthesis of glass-forming substances. The pH-metry method is rather simple and does not require costly and complicated equipment.

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